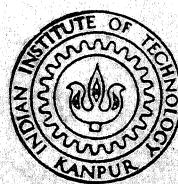


**I. PHENANTHRAQUINONE IMIDE REARRANGEMENT
II. A PHOTOCHEMICAL ROUTE TO CORANNULENES**

LAKSHMI CHARAN PADHY

CHM
1970
M
PAD
PHE



DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

I. PHENANTHRAQUINONEIMIDE REARRANGEMENT
II. A PHOTOCHEMICAL ROUTE TO CARANNULENE

A PROJECT REPORT

submitted to

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR

ACC. NO.
351

as part of
the requirements of the degree of

MASTER OF SCIENCE

Thesis
547.642
P 133p

by

LAKSHMI CHARAN PADHY

✓ CHM-1970-M-PAD-PHE

1970

Department of Chemistry
INDIAN INSTITUTE OF TECHNOLOGY KANPUR



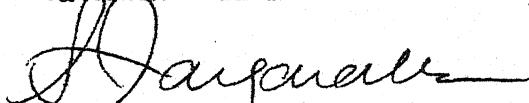
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STATEMENT

I hereby declare that the work embodied in this report is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, under the supervision of Professor S. Ranganathan.

L.C. Padhy.
(L.C. PADHY)

Statement verified


(S. Ranganathan)
Project Supervisor

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

CERTIFICATE

This is to certify that Mr. Lakshmi Charan Padhy has satisfactorily completed all the course requirements for the degree of Master of Science in Chemistry. The courses include:

Chm 401 Organic Chemistry I
Chm 402 Organic Chemistry II
Chm 404 Organic Analysis Lab.
Chm 421 Physical Chemistry I
Chm 422 Physical Chemistry II
Chm 423 Physical Chemistry Lab.
Chm 441 Inorganic Chemistry I
Chm 442 Inorganic Chemistry II
Chm 443 Inorganic Analysis Lab.
Chm 462 Instrumental Methods of Analysis (including Lab.)
Chm 500 Mathematics for Chemists I
Chm 501 Advanced Organic Chemistry I
Chm 502 Advanced Organic Chemistry II
Chm 503 Organic Preparation Lab.
Chm 521 Chemical Binding
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Chm 541 Advanced Inorganic Chemistry
Chm 600 Mathematics for Chemists II

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ACKNOWLEDGEMENTS

I avail this pleasant opportunity of expressing my deep sense of gratitude to my project supervisor Professor S. Ranganathan, who has suggested the problems, enthusiastically guided the work reported in this report and participated in many stimulating discussions of various facets of this work. With pride, I wish to make a special mention of his associations during the execution of many experiments, that have encouraged me to a great extent.

I would like to express my thankfulness to my colleagues in the Core-Laboratory whose help and cooperation at every step of this work made it smooth running. In particular I would like to thank Messers A.K. Mehrotra, B.B. Singh, H. Raman, N.C. Joshi, Ramesh Kumar, R. Vaidyanathswamy and Miss Indu Mehrotra.

My sincere thanks and appreciations are due to Messers C.S. Panda and S.K. Kar for their invaluable cooperation, encouragement and interest in this work.

The author wishes to acknowledge the much valuable assistance of Mr. A.H. Siddiqui, Microanalyst, in obtaining the Infrared spectra and Microanalyses, and R.D. Singh for having taken the strain to type out this project work.

Lakshmi Charan Padhy

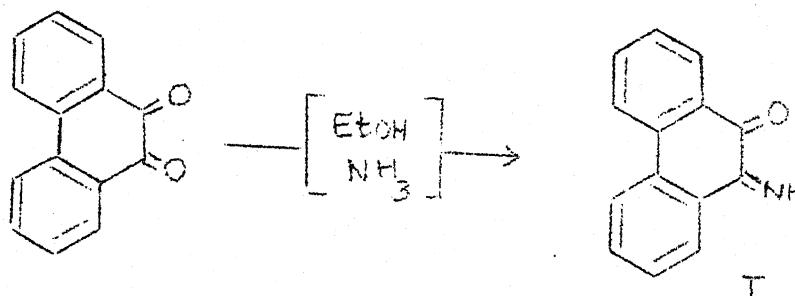
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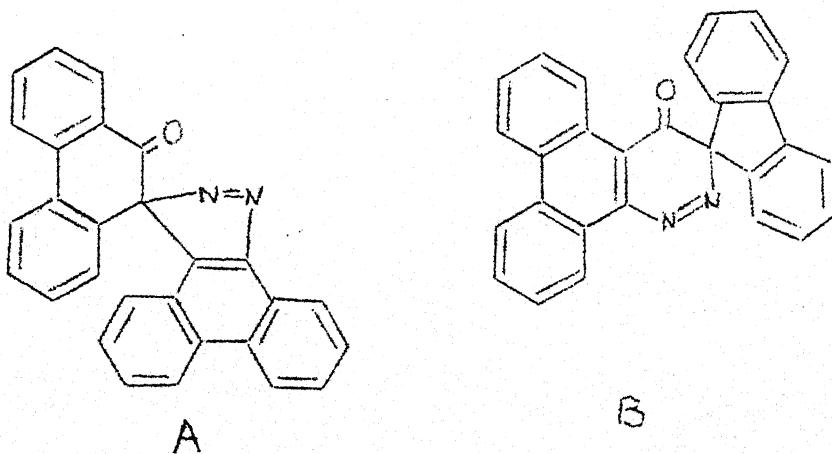
PHENANTHRAQUINONEIMIDE REARRANGEMENT

INTRODUCTION

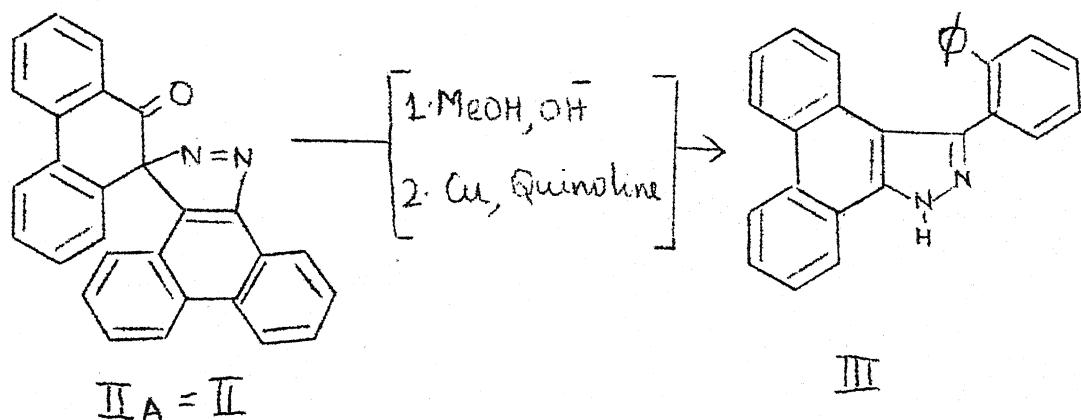
We name the extensive reorganizations associated with phenanthraquinoneimide (I) as phenanthraquinoneimide rearrangement. Compound I can be prepared by treatment of phenanthrenequinone¹ with ethanolic ammonia²:



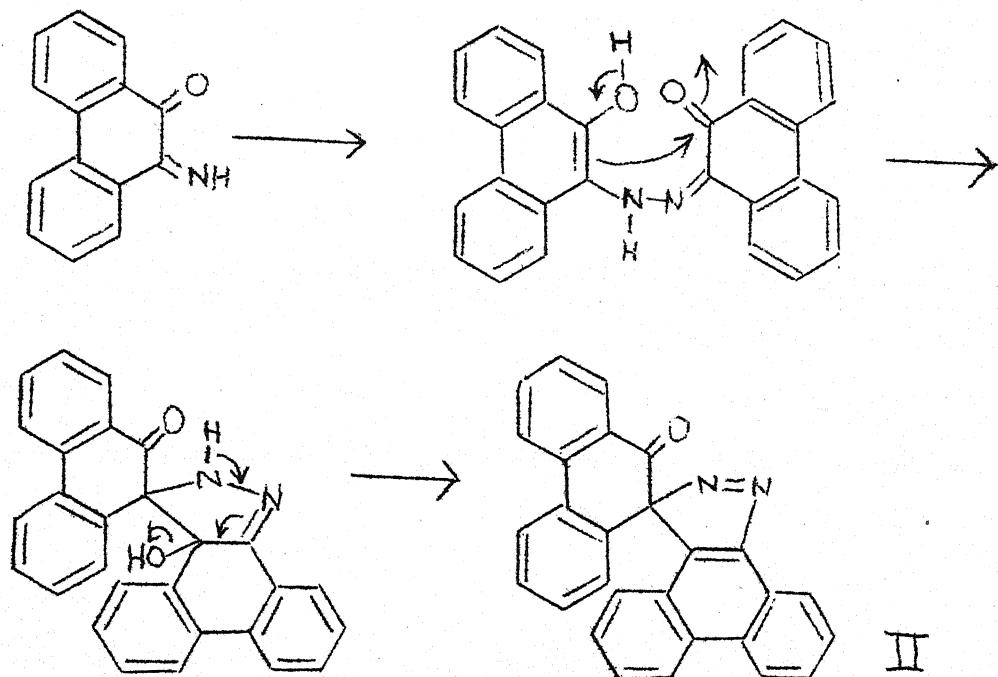
The quinoneimide I on reflux in AC₂O³ or o-dichlorobenzene⁴ loses elements of water giving rise to a compound, which since 1921³ has been referred to phenanthraquinoneimide anhydride (II). The latest effort⁵ on this problem narrowed down the possible structures for II as either A or B; however unpublished work⁴ strongly suggest a preference for A:



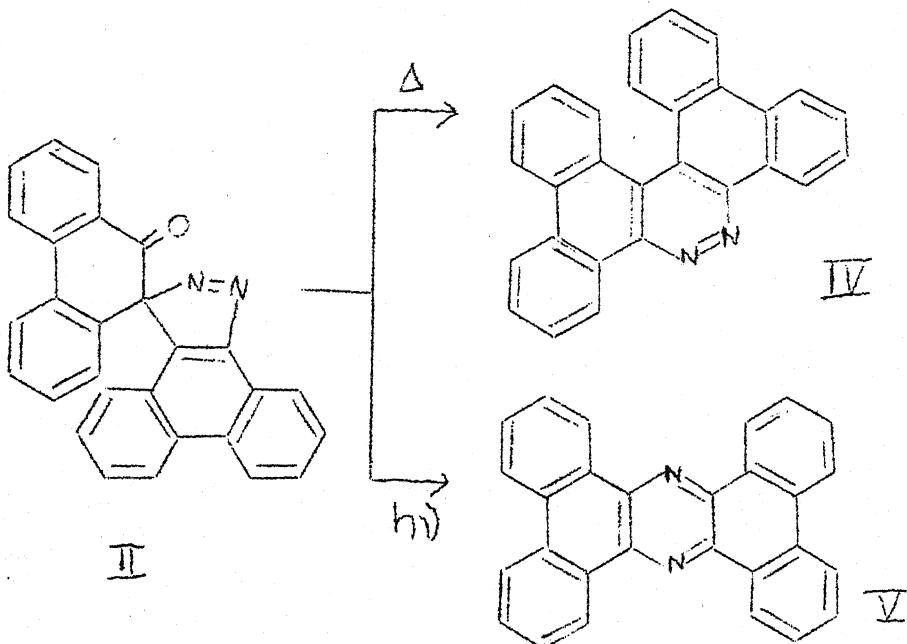
This preference is based on mechanistic reasoning as well as transformation of IIA (II) to the indazole III⁴:



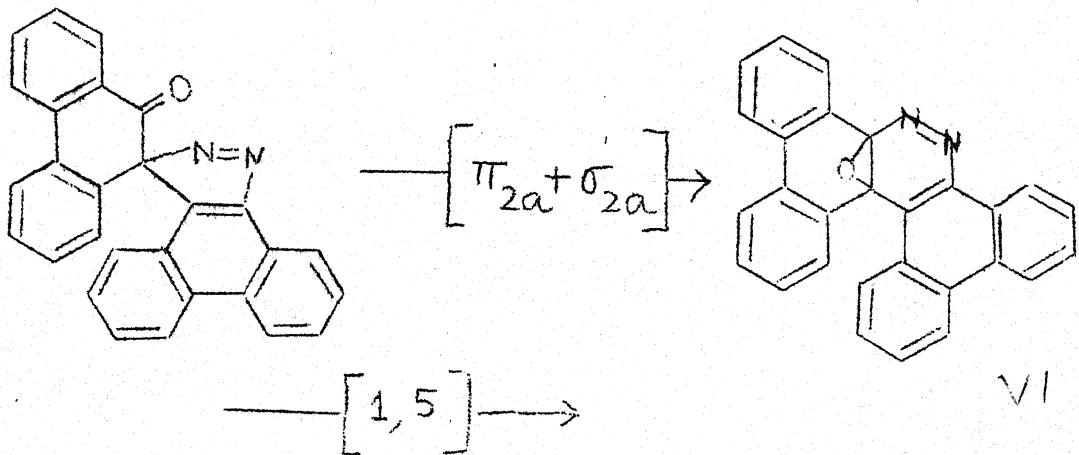
The formation of II could be readily rationalized:

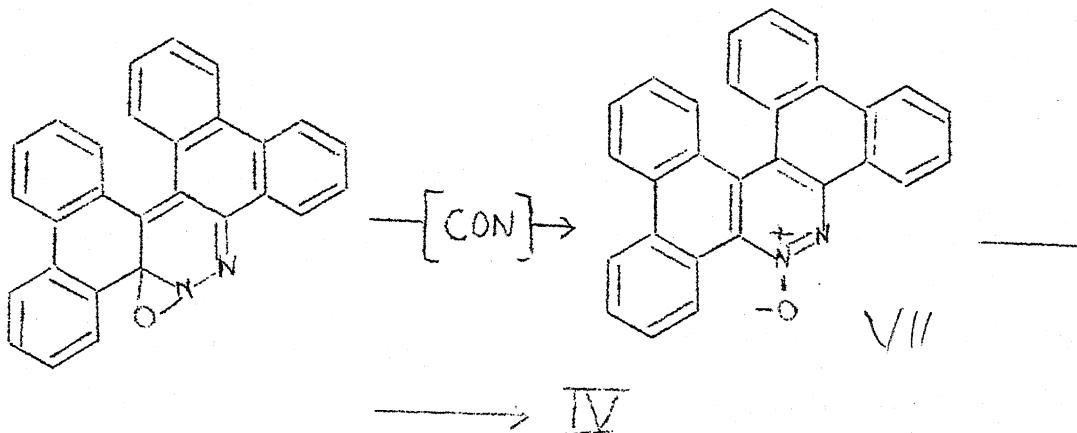


Of immense mechanistic significance is the transformation of II to the pyridazine IV thermally⁵ and to the pyrazine V photochemically⁴:

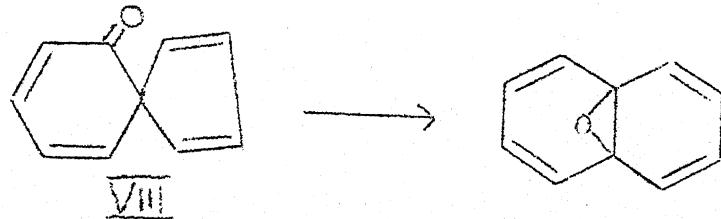


Several features of these transformations merit comment. Of primary importance is the fact that both changes involve retention of nitrogen from a system that would have been expected to lose it readily⁶ and the loss of elements of atomic oxygen which of course could not have been predicted. Then, the photolysis involves scission of a N-N double bond! The thermal change can be rationalized in terms of a series of concerted shifts.

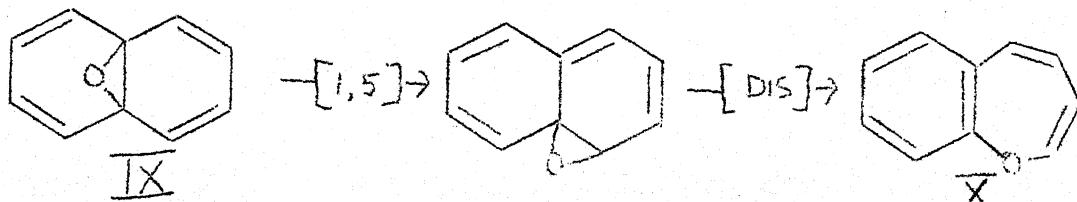




Of cardinal interest is the postulation of the intermediate VI, which as can be readily seen is a nitrogen analog of the new aromatic systems, bridged annulenes⁷. The possibility of preparation of bridged annulenes by a $\pi_{2a} + \sigma_{2a}$ process from species such as VIII is currently being explored⁸:

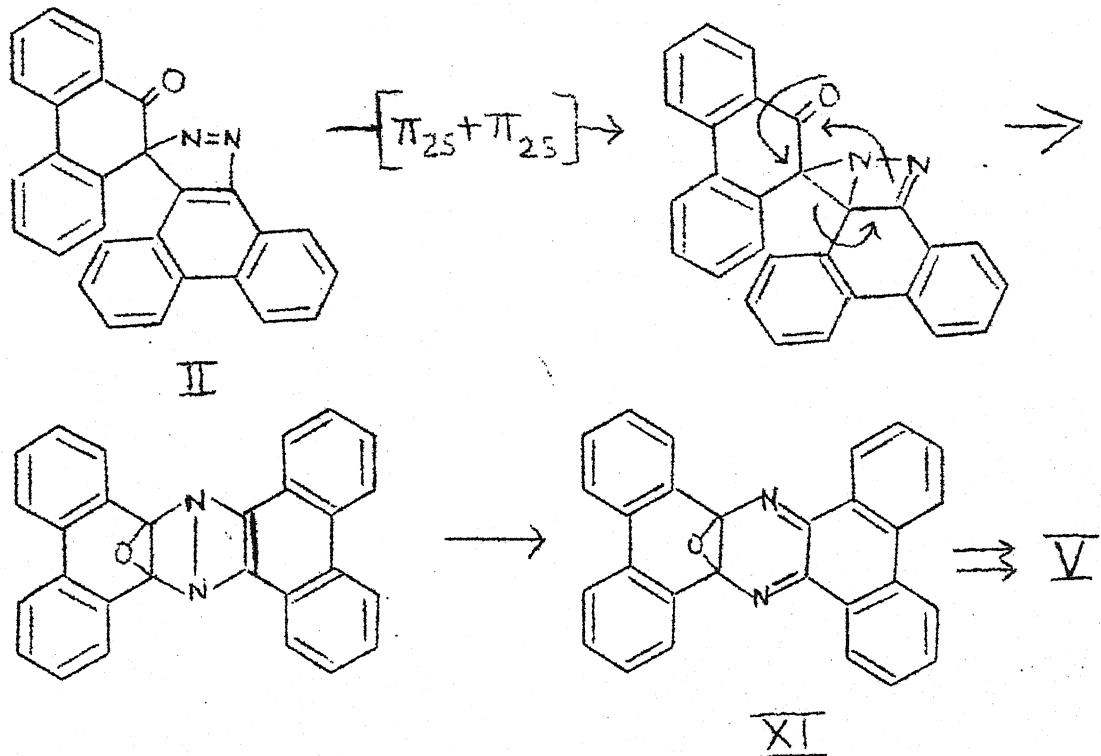


The transformation of VI to the N-oxide VII is analogous to the $\text{IX} \rightarrow \text{X}$ change⁹ and the loss of oxygen from N-oxides is not uncommon¹⁰.



The photochemical path proceeds through an initial $\pi_{2s} + \pi_{2s}$ addition

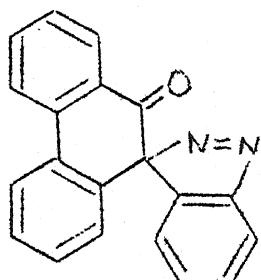
followed by changes indicated:



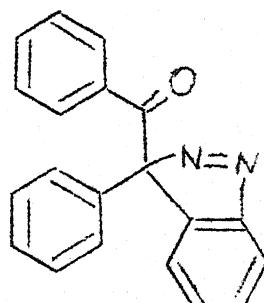
In principle, several alternate, but essentially equivalent, pathways exist for rationalization of the $\text{II} \rightarrow \text{XI}$.

PRESENT WORK

In view of the ease with which II undergoes apparently complex transformations it was considered of importance to unequivocally establish the structural assignment. Curiously we have a situation where the nature of the ultimate products are known with certainty whilst that of the starting material itself is not totally certain. The present work relates to exploratory studies dealing with preparation and transformation of model compounds XII and XIII closely related to II.



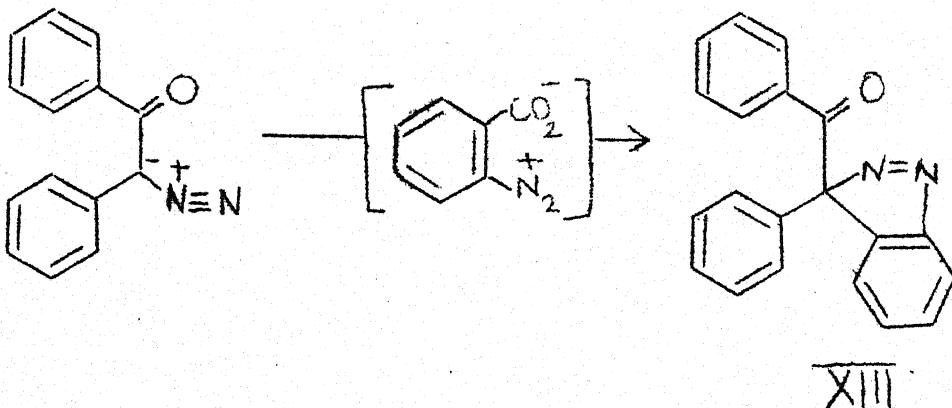
XII



XIII

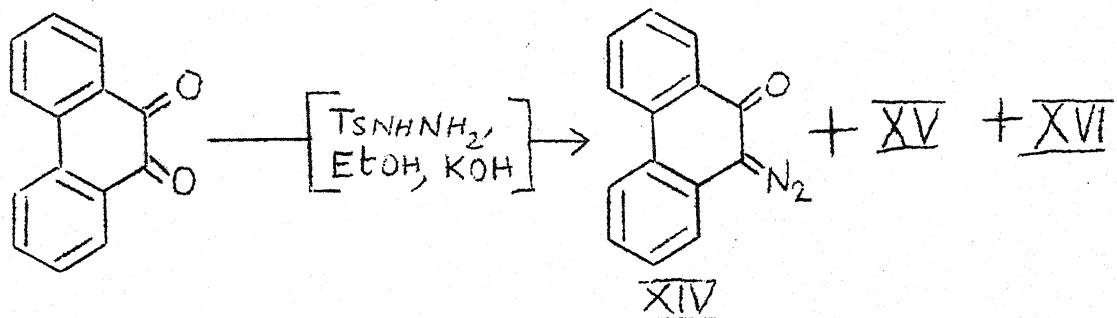
PREPARATION OF MODEL COMPOUNDS

Compound XIII is reported¹¹ and although the conditions had to be standardized could be made in high yields by insitu addition of benzyne¹² to azibenzil¹³:



In contrast the preparation of the more pertinent XII, essentially by a similar pathway, was beset with difficulties, both in the preparation of the known¹⁴ diazoketone XIV and in the subsequent reaction of XIV with benzyne.

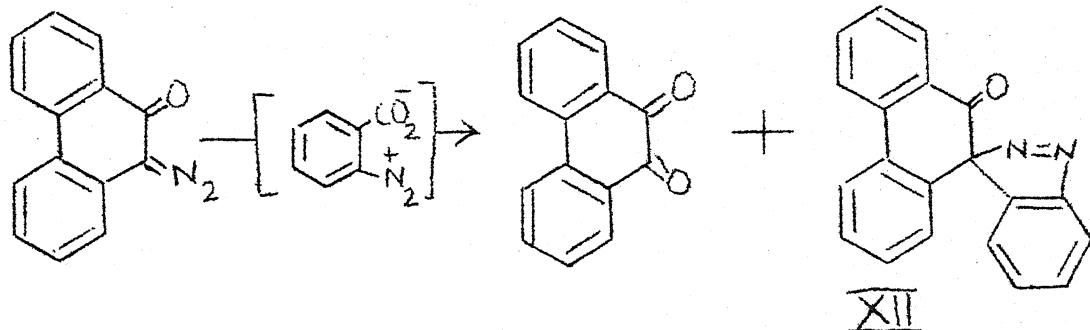
Reaction of phenanthrenequinone with p-toluene sulfonylhydrazine¹⁵ in methanol gave, in addition to XIV¹⁴, unchanged starting material, a reddish yellow compound m.p. 206-210 (XIV) a violet compound m.p. 265-270 (XVI) and few others which could not be purified. Although relevant analytical data have been obtained for these compounds no serious efforts have been made to arrive at their structures.



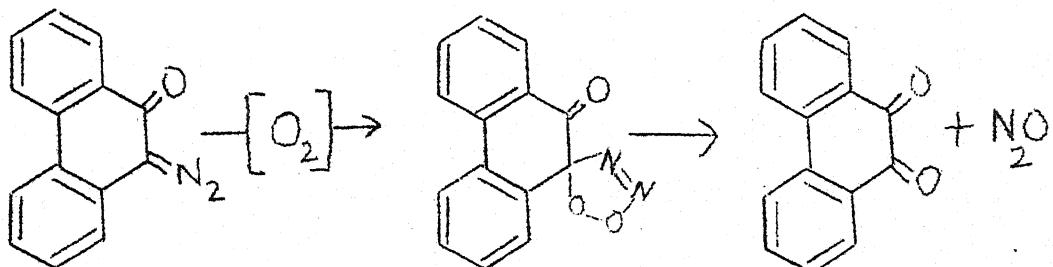
From a practical stand point the experiment, repeated several times, proved capricious; the highly coloured nature of the products posed another problem. For example, the reaction was thought to give a deep brown compound and this was ultimately analysed as phenanthrenequinone admixed with negligible amount of the violet compound (TLC)!

The insitu reaction of the diazoketone XIV with benzyne gave as the major product phenanthrenequinone along with a second compound which has been tentatively assigned the adduct structure XII on basis of

IR, UV and comparison with II:

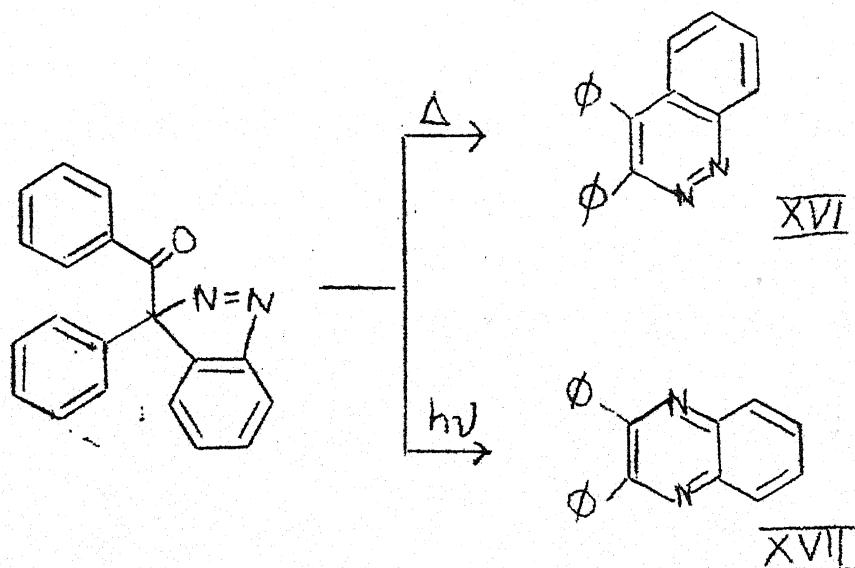


The formation of phenanthrenequinone was unexpected, but could be explained on basis of reaction of the diazoketone with oxygen.



PYROLYSIS AND PHOTOLYSIS OF THE AZIBENZIL ADDUCT XIII

On the basis of behaviour of II compound XIII could give thermally XVI and photochemically XVII:



*The alternate path involving a 1, 2 shift of either the phenyl or benzoyl group is unlike in the case of pyrazoles, not possible in XIII. Thermolysis of XIII at 300-310° for 0.25 hr. lead to formation of two major products (TLC). These were separated from unchanged starting material by extraction with ether. Evaporative distillation did not result in separation of the components; however as expected the IR spectra clearly showed as expected presence of a carbonyl free compound as the major component (IR 7). Pyrolysis with larger amounts for longer periods would be necessary to separate and identify the products.

Photolysis of adduct XIII in THF using a high pressure 450 Watt Hanovia lamp gave a mixture containing five products (TLC) and one of these correspond to authentic XVII. The identification of the products should bring to light additional fascinating facets of phenanthrenequinone-imide rearrangement.

As indicated earlier, some problems were encountered in the preparation of the known azibenzil-benzyne adduct. In order to standardize the conditions acecyclone was reacted with benzync. This reaction as expected lead to an efficient method for the preparation of the known 10,13-diphenyl-11,12-benzofluoranthene. Attempted transformation of this to a corannulene derivative is described in the next section.

EXPERIMENTAL

A. Phenanthrene-9,10-quinone was prepared by oxidation of phenanthrene with $\text{CrO}_3/\text{H}_2\text{SO}_4$, according to the procedure described¹.

I.R.- 1

B. p-Toluenesulfonylhydrazide was prepared according to procedure described².

C. REACTION OF PHENANTHRENE-9,10-QUINONE WITH p-TOLUENESULFONYLHYDRAZIDE

A mixture of phenanthrene-9,10-quinone (1 g; 5 mmole) and p-toluenesulfonylhydrazide (0.9 g; 5 mmole) was dissolved in 20 ml of 95% ethanol by refluxing in a water bath. The dark brown solution was cooled, diluted with cold water (100 ml) and made strongly alkaline by addition of dil KOH. The precipitated solid was filtered, dissolved in methylene chloride, dried, evaporated and the residue chromatographed on alumina using methylene chloride as the eluent. The diazo ketone moves as a clear yellow band. The crude XIV was crystallized from benzene and petroleum ether (40-60°).

m.p. 104-105°C yield 0.49 (36%).

I.R. - 2

Further elution with methylene chloride yielded successively unchanged phenanthraquinone and the reddish yellow compound XV; m.p. 206-210°.

Analysis , Found C, 84.53, H, 3.29. I.R.-3

T.L.C. examination showed that all the fractions were contaminated with the violet compound XVI which could be separated by preferential precipitation from cold benzene.

m.p. 267-268°.

Analysis found C, 74.80, H, 3.49, N, 6.24.

D. PREPARATION OF BENZENEDIAZONIUM-O-CARBOXYLATE¹¹

Isoamyl nitrite (4.8 ml) was added in drops to a stirred solution of crystallized anthranilic acid (2.45 g; 18 mmole) and trifluoro acetic acid (~ 3 mg) in dry tetrahydrofuran (30 ml) at 0°. After 3 hr. the precipitated salt was collected, carefully washed with cold tetrahydrofuran and dried; yield 2.29 (61%).

E. ATTEMPTED insitu ADDITION OF BENZYNE TO 9-DIAZOPHENANTHRENE-10-ONE

Benzene diazonium o-carboxylate (1.7 g; 15 mmole) added to a solution of the ~~the~~ -diazoketone in dry methylenechloride (25 ml) and the heterogeneous mixture refluxed (5 hr). The dark reaction mixture was evaporated and the residue chromatographed on alumina using benzene as an eluent to give successively phenanthraquinone and a compound m.p. 176-180 believed to be the desired XII. I.R. - 4.

F. PREPARATION OF AZIBENZIL¹³

Benzilmonohydrazone (7 g; 32 mmole), yellow mercuric oxide (10.2 g) and anhydrous magnesium sulphate (4.5 g) were suspended in dry ether (35 ml) and stirred at 45°. After 4 hr the solution was filtered and evaporated to give orange yellow crystals of azibenzil; yield 2.89 g (40%), m.p. 76°.

A better procedure is to shake for 0.25 hr a mixture of benzilmonohydrazone (7 g; 32 mmole), yellow mercuric oxide (10.2 g), anhydrous magnesium sulphate and 2 drops of 25% KOH in dry ether (35 ml). Filtration and evaporation of the solution gave orange yellow crystals of azibenzil; m.p. 77-78°, yield 5.68 g (80%).

G. insitu BENZYNE ADDITION TO AZIBENZIL: PREPARATION OF XIII:

Benzene diazonium α -carboxylate (0.44 g; 3 mmole) was added to a solution of azibenzil (0.679; 3 mmole) in dry methylene chloride (15 ml). The mixture was refluxed for 8 hr. The solvent was removed and the residue chromatographed on alumina using benzene as an eluent. The crude 3-phenyl, 3-benzoyl indazole XIII was crystallized from methanol; m.p. 168° (literature (M) 167°); yield 0.601° (67%), I.R. - 5 & 6.

H. THERMOLYSIS OF 3-PHENYL, 3-BENZOYL INDAZOLE

The indazole XIII (0.17 g; 0.6 mmole) was immersed in a preheated (300-310°) silicone bath and kept for 0.25 hr. The crude product was extracted with ether and the ether extract evaporatively distilled. The distillate showed preponderance of a carbonyl free component, I.R.-7.

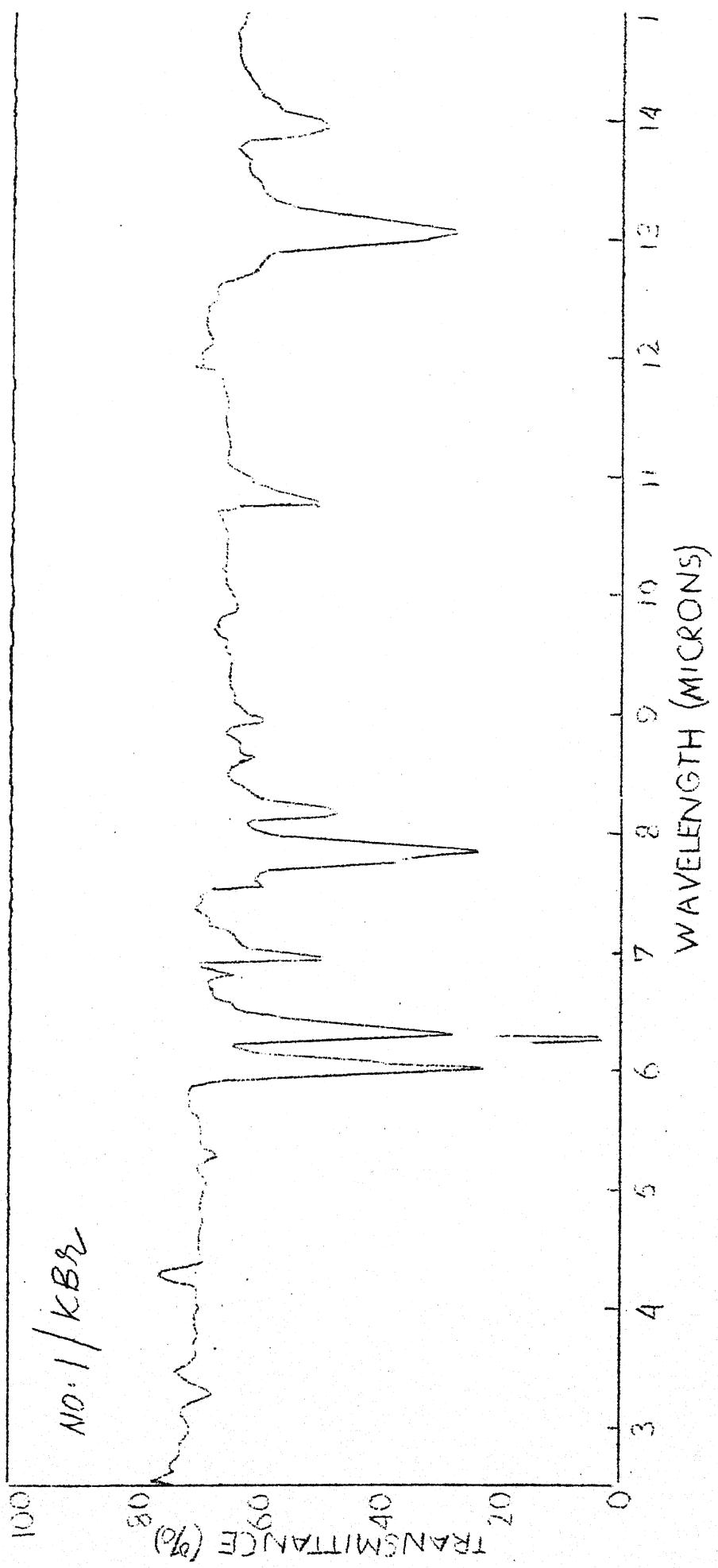
I. PHOTOLYSIS OF 3-PHENYL, 3-BENZOYL INDAZOLE

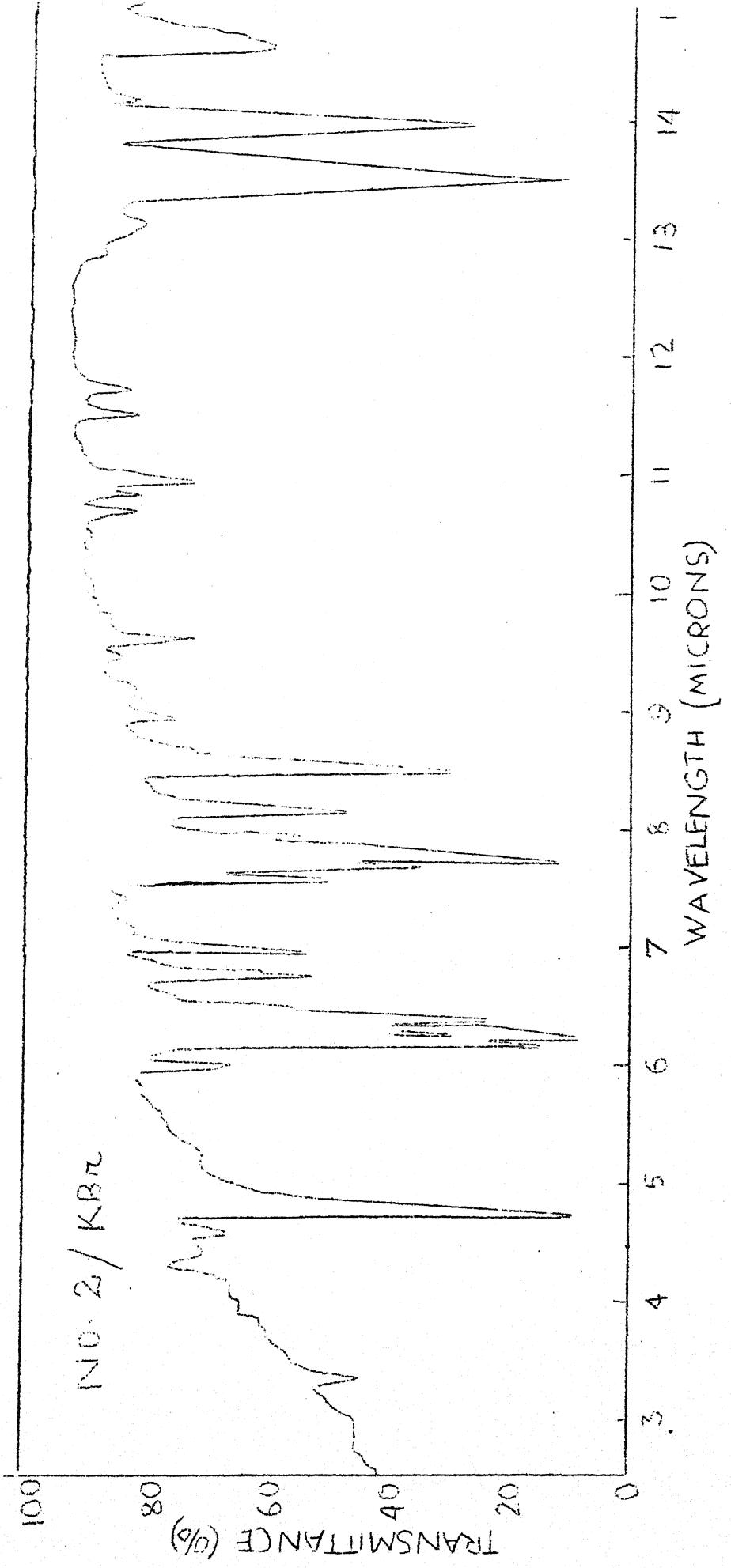
A solution of the indazole (0.264 g;) in dry tetrahydrofuran (350 ml) was photolyzed for 5 hr using a Hanovia 450 watt high pressure mercury vapour lamp with a vycor filter. The solvents were evaporated and residue extracted with petroleum ether (40-60°) to remove unchanged starting material. The petroleum ether extract was evaporated and the T.L.C. developed from a system of benzene ethylacetate (9:2) showed the presence of atleast 5 major components; further one of these spots was identical to that of authentic diphenyl quinoxaline XVII.

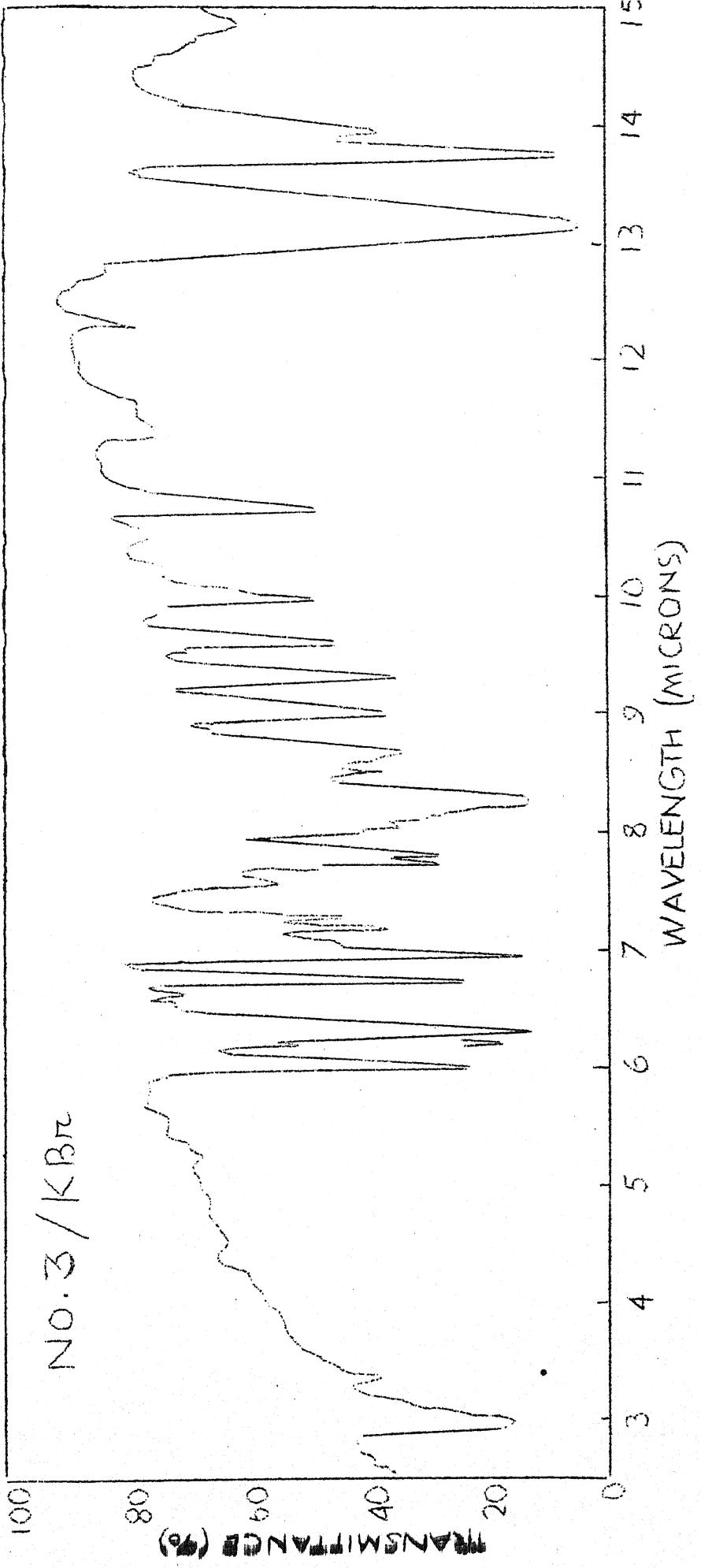
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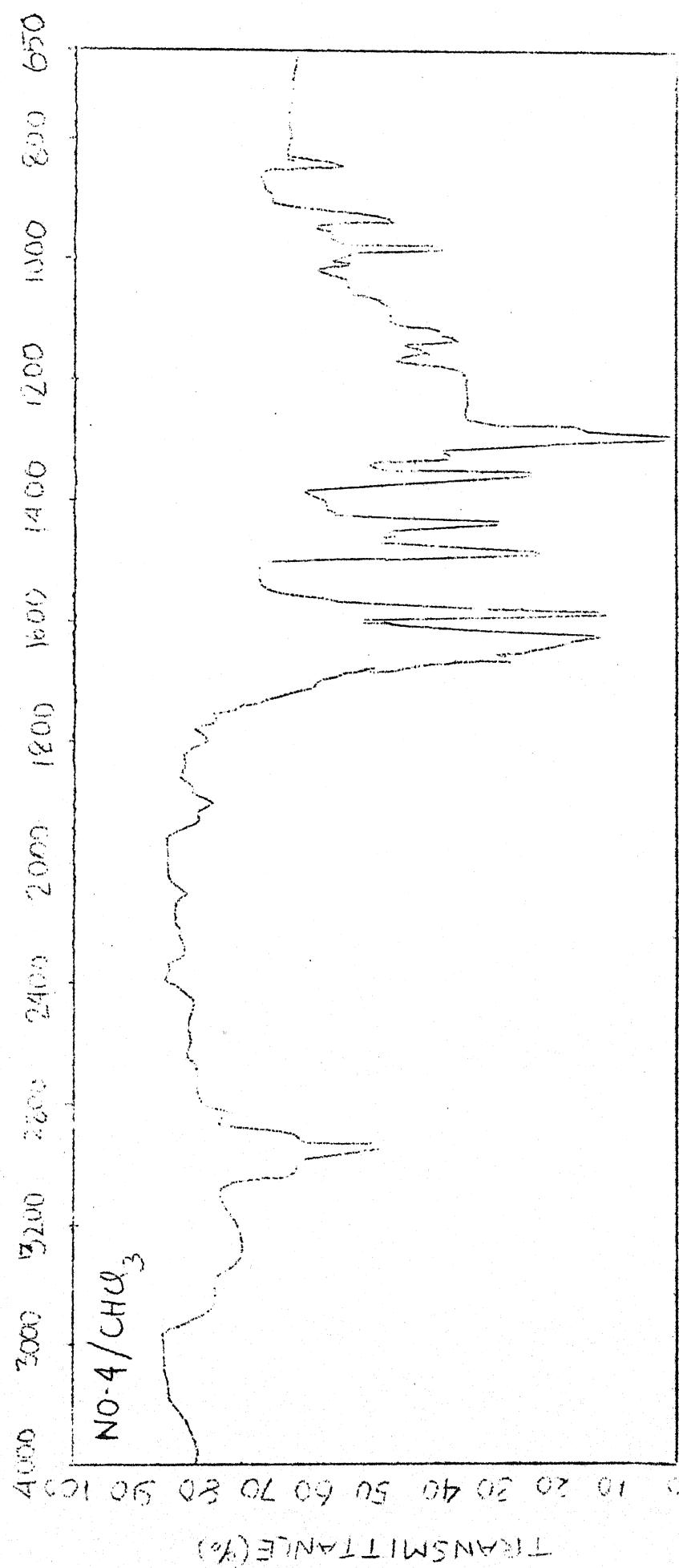
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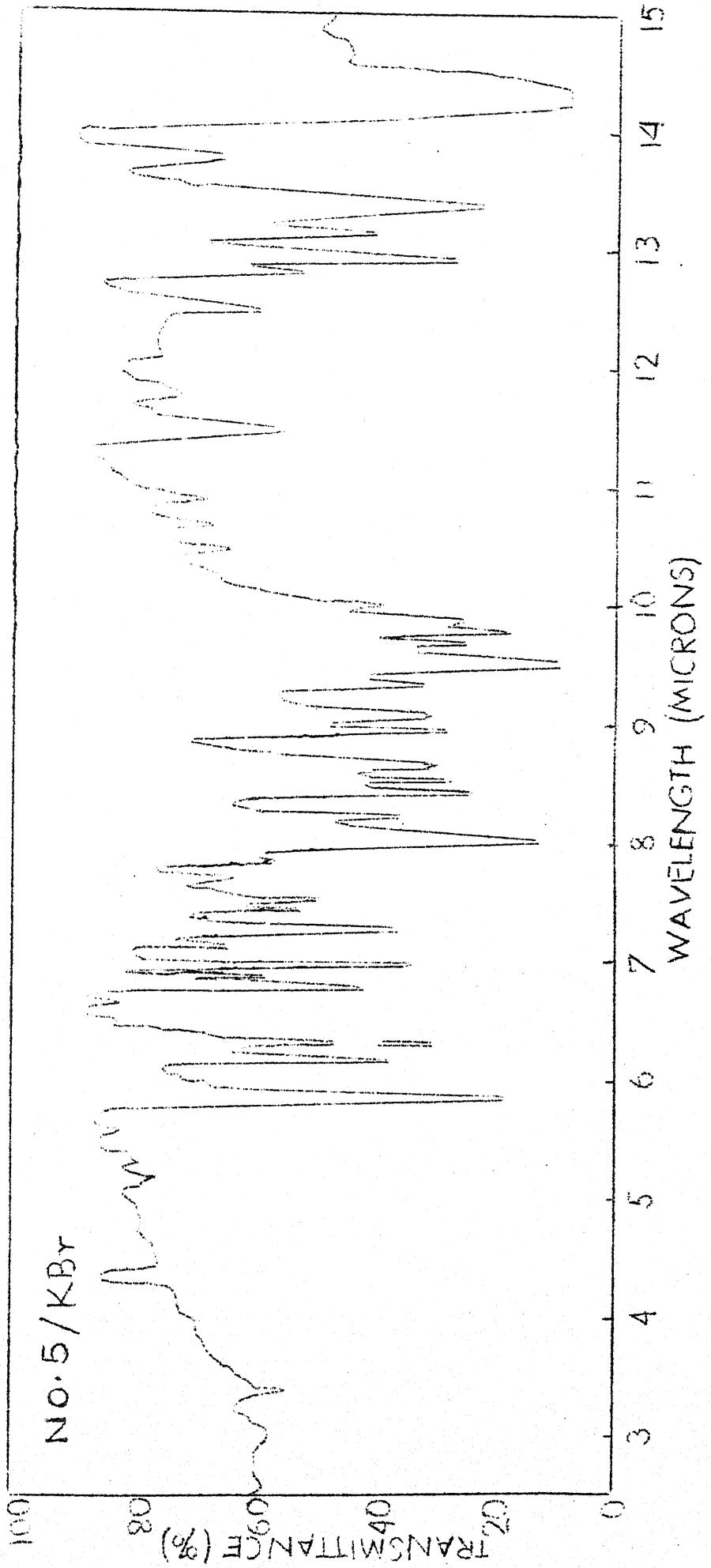
INFRARED SPECTRA

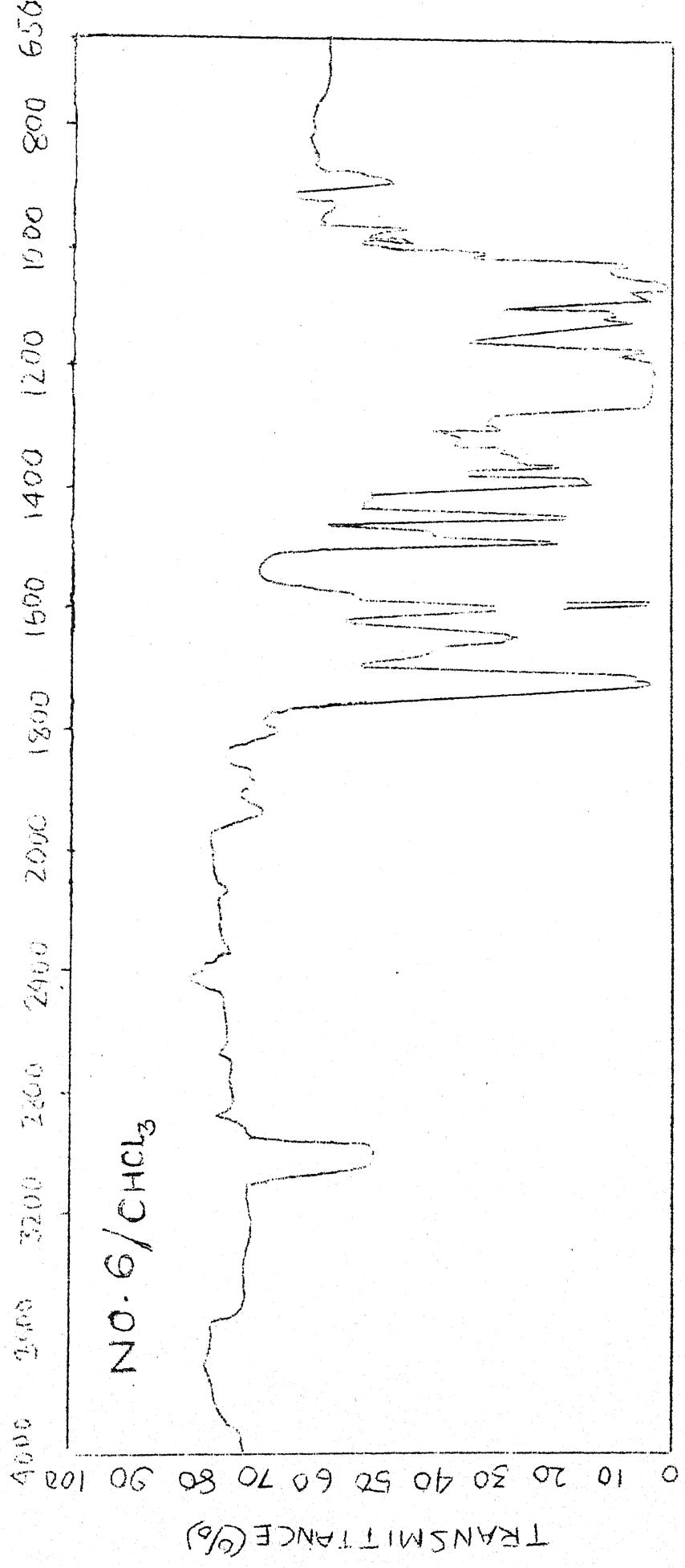




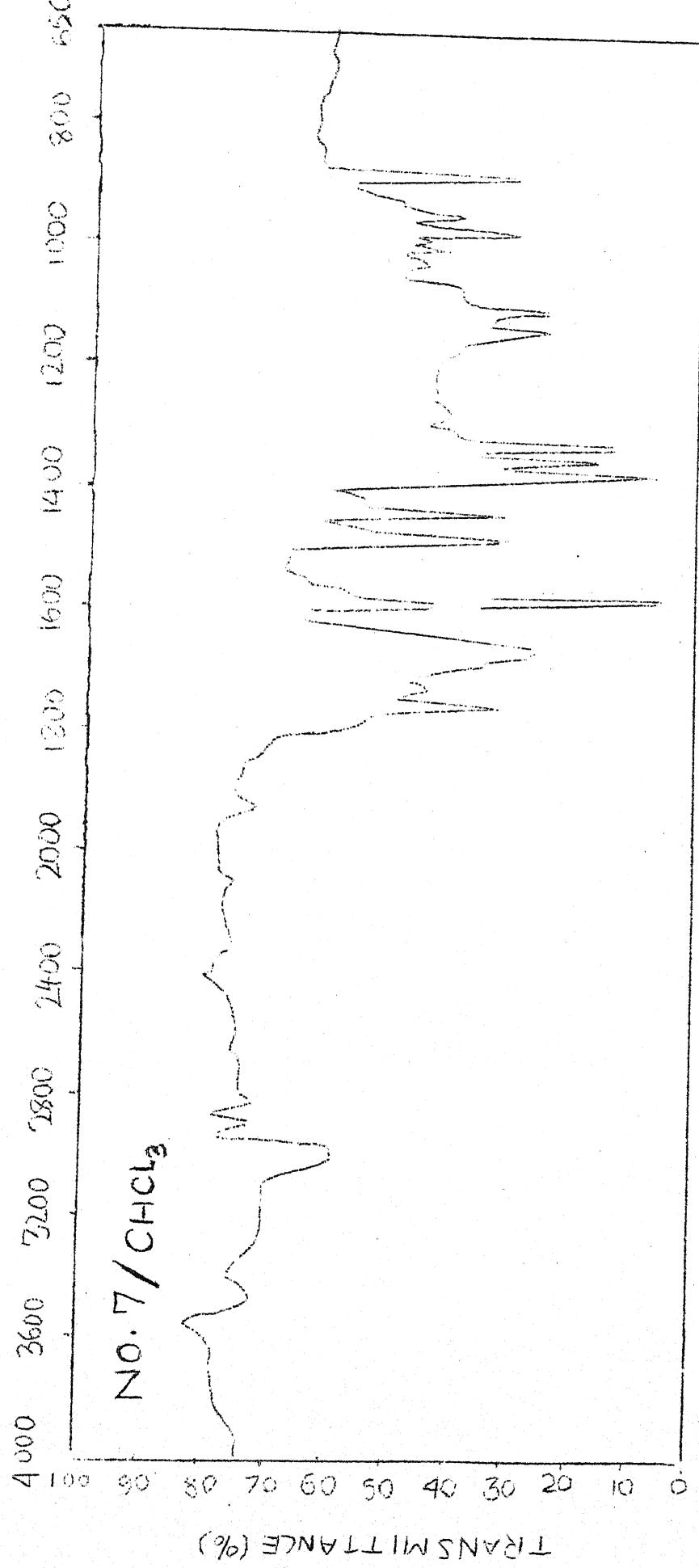








TRANSMITTANCE (%)



TRANSMITTANCE (%)

PHOTOCHEMICAL ROUTE TO CORANNULENE

1. **Introduction**

Corannulene is a polycyclic aromatic hydrocarbon consisting of a central benzene ring fused with three annulene rings. It is a highly stable and unique molecule with a complex electronic structure. The photochemical route to corannulene involves the photolysis of a substituted benzene derivative, such as a substituted benzene derivative, to form corannulene. This route is a relatively simple and efficient way to synthesize corannulene, and it has been used by many researchers to study the properties of this molecule.

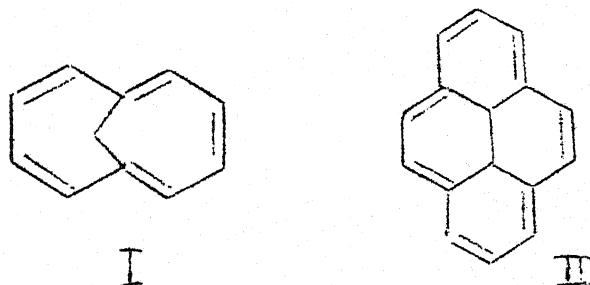
2. **Experimental Procedure**

The experimental procedure for the photochemical route to corannulene involves the following steps:

1. Preparation of the starting material: A substituted benzene derivative is prepared, typically by a Friedel-Crafts reaction or a Grignard reaction.
2. Irradiation: The starting material is irradiated with ultraviolet light (e.g., 365 nm) in the presence of a photosensitizer (e.g., benzophenone) and a solvent (e.g., benzene).
3. Isolation: The product is isolated by column chromatography or recrystallization.
4. Characterization: The product is characterized by spectroscopic methods (e.g., NMR, IR, mass spectrometry) and elemental analysis.

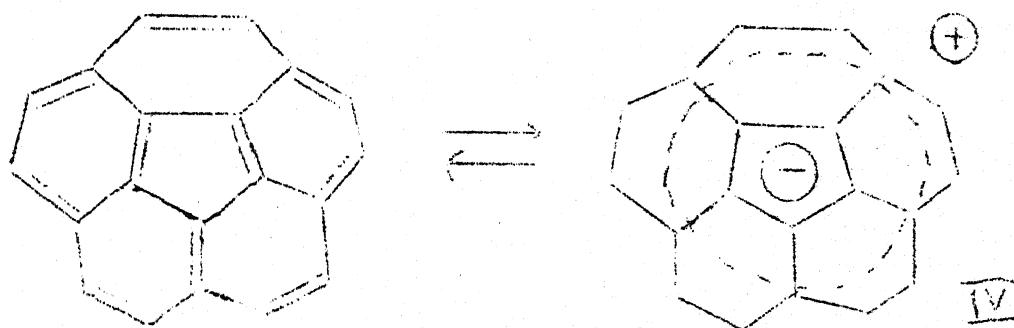
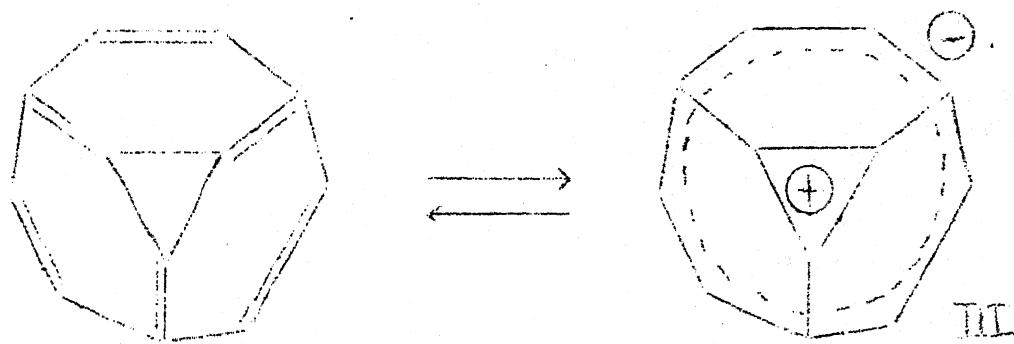
INTRODUCTION

Severe H-H interactions prevent the immediate $4n + 2$ homologs of benzene, starting with cyclodecapentaene, assuming coplanarity, a condition that is essential for gainful overlap. Attempts to alleviate consequences of this unfavourable interaction has lead to an array of new type of aromatic compounds represented by the bridged systems I and II^{1,2}

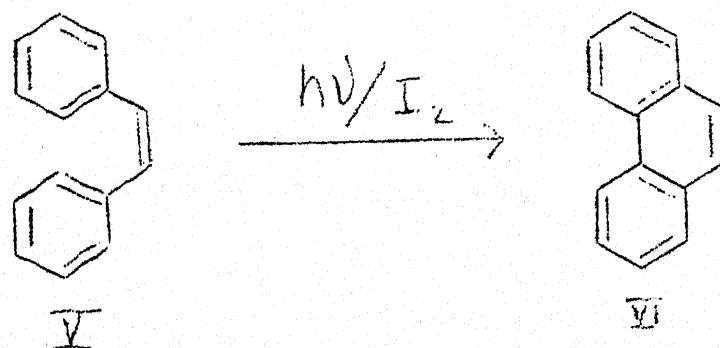


In these compounds the core lies in a different plane and therefore is isolated from the π system.

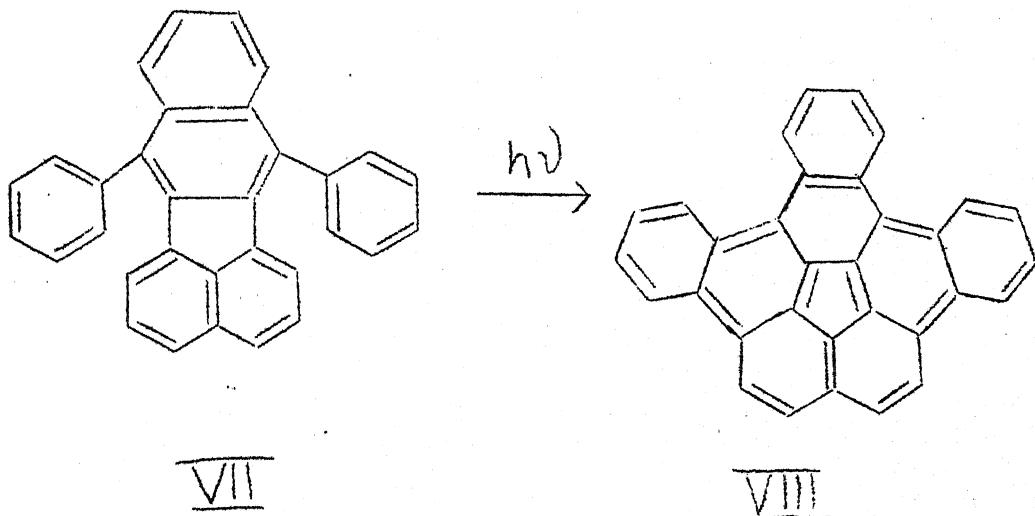
An alternate approach would be to build a polyene system around a cyclic core. The smaller the size of the core the greater will be the strain produced by the girdle and consequently the inner ring would be more isolated from the rim. In compounds such as III, IV this isolation could be facilitated by separation into two aromatic species:



Compound IV has been synthesized in a classical manner involving several steps³ and is named corannulene. There is no evidence for extensive polarization in IV; in contrast the radial anion does indeed have a bowl configuration⁴. The photochemical stilbene-phenanthrene cyclization V → VI has been employed in efficient synthesis of helicenes⁵.

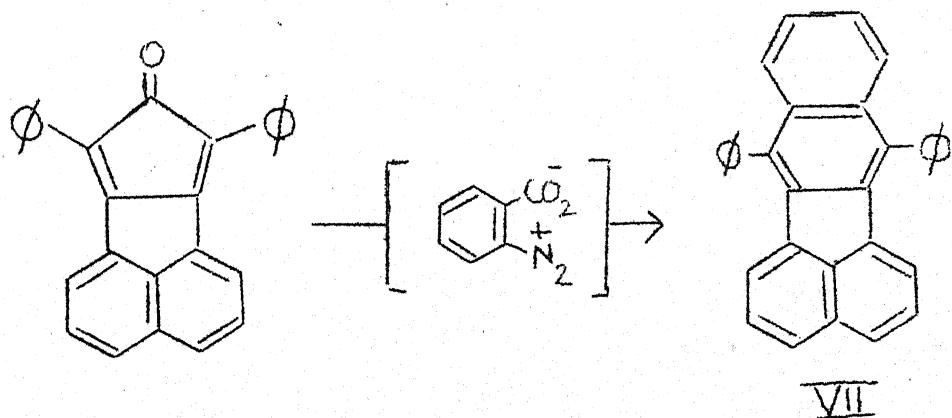


Systematic efforts are being made to use this principle in the construction of series represented by III and IV⁶; however the ready availability of VII (please see earlier section) made the photolytic transformation to the tribenzocorannulene VIII a tempting proposition.



PRESENT WORK

Compound VII⁷ was prepared in quantitative yields by in situ addition of benzyne to acecyclone:



Photolysis of VII employing a high-pressure 450 watt lamp in cyclohexane-iodine as well as in benzene-iodine failed to yield any products. In view of the ease with which similar cyclizations have been done the failure is inexplicable.

EXPERIMENTAL

PREPARATION OF 10,15-DIPHENYL-11,12-BENZOFUORANTHENE VII:

Benzene diazonium-o-carboxylate (0.22 g; 1.5 mmole) was added to a solution of acecyclone (0.36 g; 1 mmole) in dry methylene chloride (25 ml). The mixture was refluxed for 10 hr (discharge of violet acecyclone colour). The solvents were removed and the crude fluoranthene was crystallized from benzene.

m.p. 264° (lit. 267°); yield 0.394 g (97.5%); I.R. - 8.

ATTEMPTED SYNTHESIS OF TRIBENZOCORANNULENE

A solution of the 10,15-diphenyl-11,12-fluoranthene (0.5 g; 1.25 mmole) and resublimed iodine (18 mg) in dry benzene was photolyzed using Hanovia 450 watt high pressure mercury vapour lamp with a vycor filter for 10 hr and 20 hr in two separate experiments; however, m.p., I.R. and U.V. indicate no change.

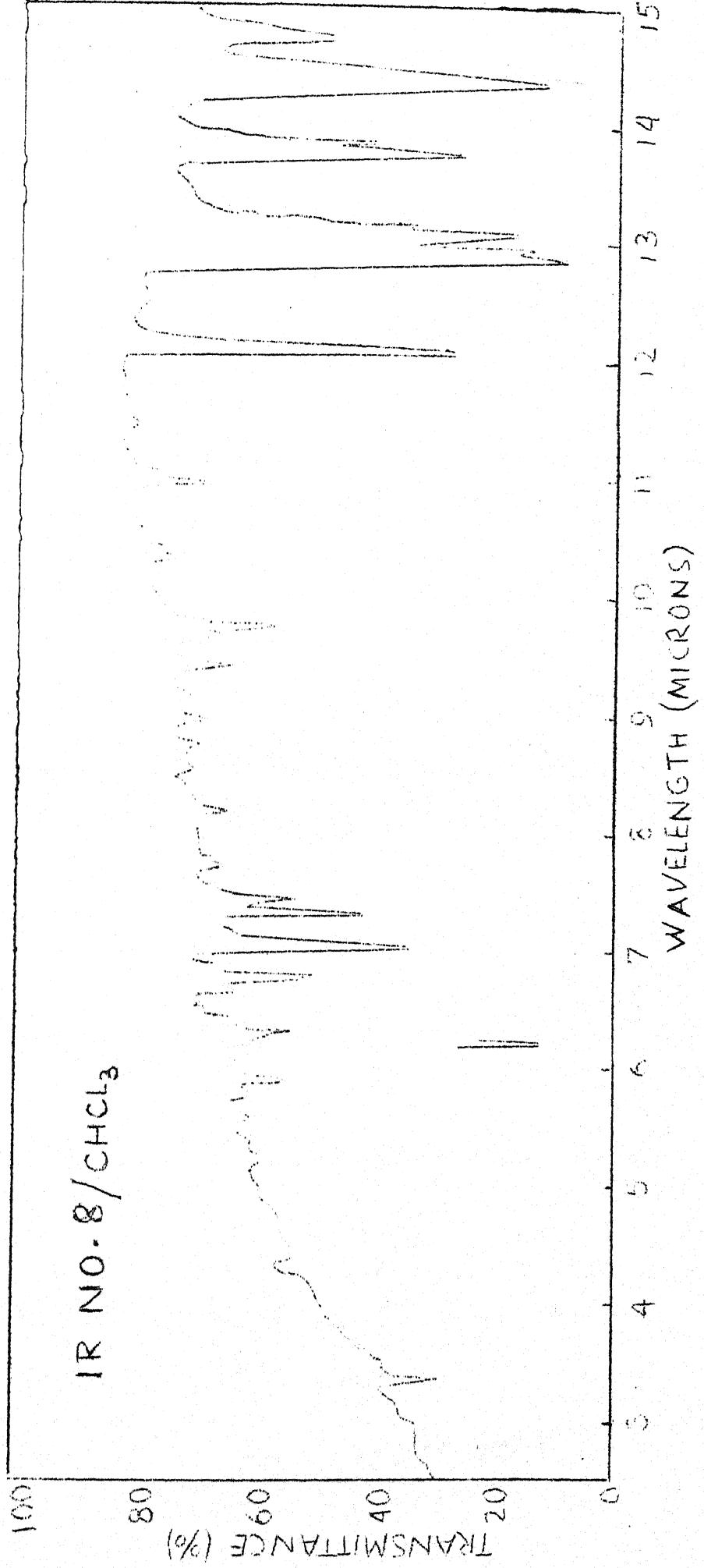
Photolysis in cyclohexane using a vycor filter for 6 hr showed no formation of new products.

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VITAE

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